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Experimental magnetization evidence for two superconducting phases in Bi bicrystals with large crystallite disorientation angles

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Magnetization measurements prove that the magnetic properties of large-angle ($\theta > 30°$) bismuth bicrystals with a crystallite interface (CI) of twisting types essentially differ from well-known results on single-crystalline specimens. Two superconducting phases with $T_c \sim 8.4$ K and ~ 4.3 K were observed at the CI of bicrystals while ordinary rhombohedral Bi is not a superconductor. We conclude that these phases have to do with the central part and the adjacent layers of the CI of bicrystals.

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I. INTRODUCTION

Magnetic properties of bismuth have been intensively studied for a long time. This interest is caused by two reasons. First, in bismuth the de Haas–van Alphen effect was found,[1] which later on was used for the Fermi surface determination almost in all metals and alloys. Second, the monotonic part of the magnetic susceptibility in Bi is by an order of magnitude higher than in metals. In spite of the fact that the doubled ratio of the spin to orbit splitting of the energy levels of electrons is close to 2 and according to the Pauli-Landau formula susceptibility χ must be above zero, Bi shows anomalous diamagnetism.

Charge carriers in Bi energy bands in weak magnetic fields give paramagnetic contributions, hence when their concentration is high the diamagnetism decreases with the increasing chemical potential. The susceptibility as a function of the chemical potential has peculiarities connected with the Fermi surface topology, which become smooth at finite temperatures, when the interaction of the charge carriers with each other or with impurities is intensified.[2] These processes must manifest themselves most clearly in bicrystal samples, where, in the region of an inner boundary, significant changes in the electron energy spectrum take place,[3–5] the charge carrier density is increased, the charge carrier interaction with the inner boundary varies, etc.

In this work we present results of magnetic moment measurements of bismuth bicrystals (consisting of two single-crystalline blocks and the crystallite interface), which show evidence of two superconducting phases associated with interfacial regions, while the bulk of the crystals does not exhibit superconductivity.

II. EXPERIMENTAL PROCEDURE

Bi bicrystals of a twisting type are obtained by the zone recrystallization method using the double seed technique. Samples for measurements were prepared in the form of parallelepipeds ($1 \times 2 \times 4$ mm^3) and showed a clearly pronounced large-block structure with blocks (crystallites) being disoriented relative to each other. In one of the crystallites [for example, crystallite A in Fig. 1(a)] the bilayers (the crystal structure of the bismuth has a layered character) are laid perpendicular to the axis C_3 ($C_3 \| n_A$), and in the other (crystallite B) the normal to the bilayer plane and the direction of the first crystallite axis C_3 make up an angle up to 30°. The crystallite interface (CI) represents a single-crystalline platelet (a share of the CI volume from an overall volume of a bicrystal $\sim 10^{-4}$) with the width estimated by means of the scanning electron microscopy (SEM) of about 100 nm [Fig. 1(b)]. By a degree of perfection the CI can be compared only to a surface cleaved in deep vacuum. The width of CI also was appreciated by a value of a magnetic field when quantum oscillations become observable.[6] For a field applied parallel to the interface plane the spectrum of the Hall resistance quantum oscillations of bicrystals contains two new harmonics, frequencies of which essentially differ from the values characteristic of single-crystal samples [see Fig. 1(c)]. One of these harmonics with a frequency five times higher than the cross-sectional area of a Fermi surface of Bi are observed at $H > (20 \div 25)$ kOe. A calculation of the cyclotron orbit diameter corresponding to these fields correlates with the width of the CI, which was determined by means of the SEM. The second component with a frequency almost twice as high as the first one is visible at $H > 100$ kOe. The diameter of cyclotron orbits of charge carriers corresponding to this field is ~ 60 nm. We speculate that this value characterizes the thickness of the central layer of the interfacial region, resulting from a well-known fact, that the CI is complex systems consisting of a solitary central part and two similar adjacent layers on both sides of it. The central and both adjacent layers of CI are characterized by specific peculiarities of the Fermi surface, a different density of the charge carriers, structural changes of crystal lattices, etc. By frequencies of the quantum oscillations of the Hall resistance, the density of charge carriers in the central part of the CI of the investigated bicrystals makes $\sim 2.5 \times 10^{20}$ m^{-2}, in adjacent layers $\sim 1.2 \times 10^{20}$ m^{-2}. The bicrystals had p-type

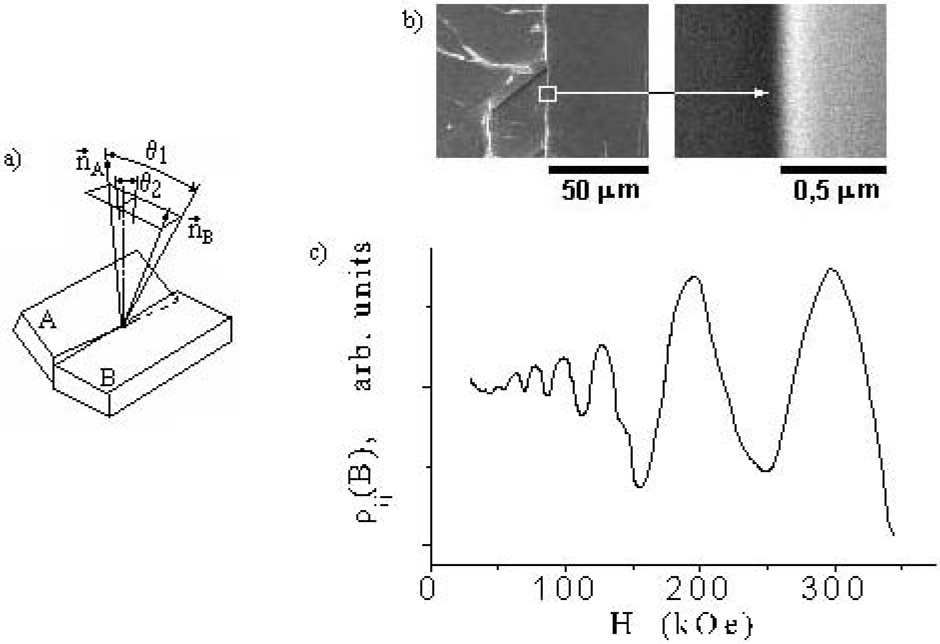

FIG. 1. (a) Schematic representation of bismuth bicrystals with crystallite interfaces of a twisting type. *A*, *B*, crystallites; θ_1, relative CI disorientation angle; θ_2, rotation angle in an interface plane. (b) SEM, images of CI of Bi bicrystals with $\theta_1=29°$, $\theta_2=11°$. (c) The quantum oscillations of the Hall resistance in Bi bicrystals with $\theta_1=29°$, $\theta_2=11°$ at 4.2 K, and a magnetic field directed along the inner boundary plane (the monotonic part has been subtracted).

conductivity and were of special interest because the CI exhibits superconducting properties [for some samples $T_{\text{onset}} \sim 16$ K (Ref. 4)].

The magnetic moment of these bicrystals was studied in the temperature range (1.8–300 K), and in the fields up to 70 kOe using a Cahn balance, a superconducting quantum interference device magnetometer (Quantum Design), and the physical property measurement system. The measurements were carried out in the International Laboratory of High Magnetic Fields and Low Temperatures (Wroclaw, Poland), the Institute of Low Temperatures and Structure Research of the Polish Academy of Sciences in Wroclaw (Poland), and the Institute for Solid State and Material Research (Dresden, Germany).

III. TEMPERATURE DEPENDENCE OF MAGNETIZATION

Figure 2 shows the examples of temperature dependences of the static magnetic moment of Bi bicrystals with the CI of the twisting type. At low temperatures two superconducting phases are observed: one has the transition temperature $T_c \sim 8.4$ K, and the other $T_c \sim 4.3$ K.

The existence of superconducting phases with different critical temperatures means that at CI, alongside with other phenomena (changes of the electron-phonon interaction, electron-electron repulsion, free path length of charge carriers, etc.), appreciable changes of the density of Cooper pairs at distances comparable with the coherence length are taking place.

A superconducting phase with the transition temperature $T_c \sim 8.4$ K was earlier described in Refs. 3 and 4, where it was established that the upper critical field is equal to $H_{c2} \sim 25$ kOe, coherence length $\xi(0) \sim 12$ nm, and energy gap $2\Delta(0) \sim 3.3$ meV. The coherence length $\xi(0)$ in this superconducting phase is much smaller than the width of the central part of CI ($d_1 \sim 60$ nm), so the adjacent layers do not improve conditions for the correlation of the Cooper pairs in the central part of the crystallite interface.

On the other hand, the thickness of the adjacent layers of bicrystals CI was estimated to be about $d_2 \sim 20$ nm. They border the Bi normal phase (the width of crystallites greatly exceeds the coherence length). The charge carrier concentration in these layers is approximately twice lower than in the central layer and is by three orders of magnitude higher than in single-crystalline thin Bi films. Therefore, the transition temperature T_c in adjacent layers must be quite strongly suppressed by proximity effects of the single-crystalline bismuth.

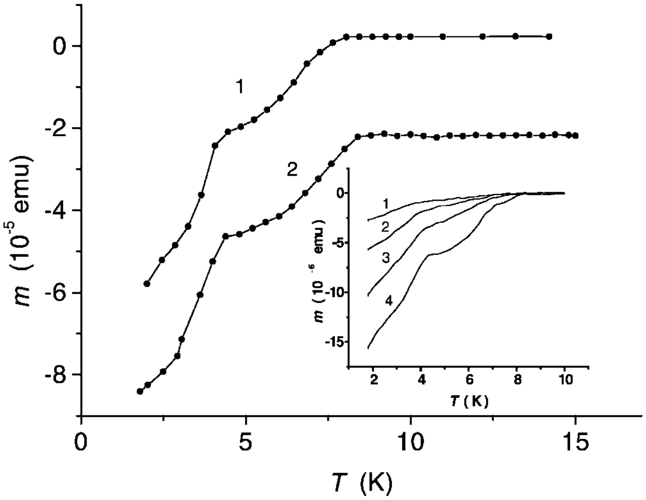

FIG. 2. Temperature dependences of a magnetic moment of Bi bicrystals with the CI of the twisting type. 1, $\theta_1=29°$; $\theta_2=11°$; 2, $\theta_1=62°$, $\theta_2=2°$; 1, 10 Oe; 2, 20 Oe. Inset: Temperature dependences of a magnetic moment at different applied magnetic fields in Bi bicrystals with $\theta_1=29°$, $\theta_2=11°$; 1, 1000 Oe; 2, 300 Oe; 3, 100 Oe; 4, 0 Oe. The magnetic field is directed along the inner boundary plane.

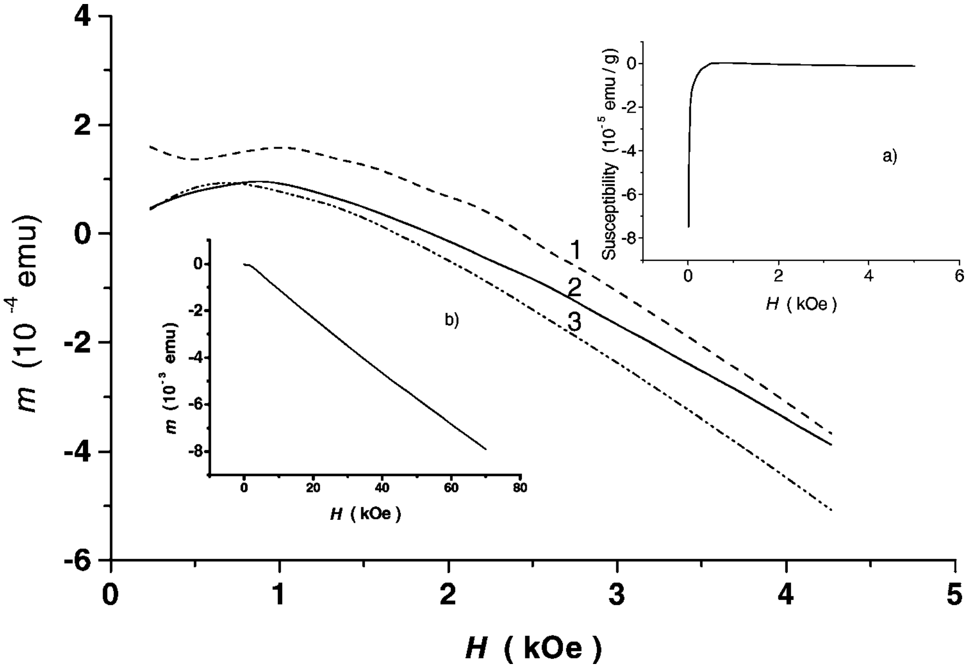

FIG. 3. Field dependences of a magnetic moment of Bi bicrystals with CI of the twisting type ($\theta_1 = 62°$, $\theta_2 = 2°$). 1, 4.2 K; 2, 300 K; 3, 77 K. Inset (a): Field dependence of a magnetic susceptibility at $T = 1.8$ K of Bi bicrystals with $\theta_1 = 62°$, $\theta_2 = 2°$. Inset (b): Field dependence of a magnetic moment at $T = 2$ K of Bi bicrystal with $\theta_1 = 29°$, $\theta_2 = 11°$.

From the temperature dependences of the ac magnetic moment measured in the magnetic field orientated along the inner boundary plane (in crystallites this direction corresponds to $H \| C_3$, Fig. 2, inset) the upper critical field $H_{c2}(T)$ is determined for the superconducting phase with $T_c \sim 4.3$ K (for the phase with $T_c \sim 8.4$ K this parameter is determined in Ref. 3). The slope of the $H_{c2}(T)$ dependence is estimated to be equal to $dH_{c2}/dT \sim 5.5$ kOe/K. The evaluation of $H_{c2}(0)$ was carried out by the formula[7]

$$H_{c2}(0) = -0.69 T_c (dH_{c2}/dT). \tag{1}$$

As a result, it is found that $H_{c2}(0) \sim 16.6$ kOe, and the coherence length $\xi(0) \sim 14$ nm [it is determined from the relation $\xi^2(0) = \Phi_0 / 2\pi H_{c2}(0)$, where $\Phi_0 = 2.07 \times 10^{-7}$ G cm^2].

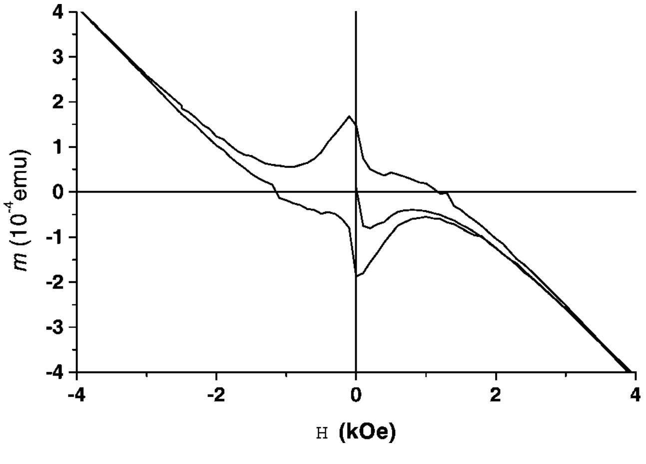

FIG. 4. Magnetic hysteresis loop at $T = 2$ K of Bi bicrystals with $\theta_1 = 29°$, $\theta_2 = 11°$. The magnetic field is orientated along the inner boundary plane.

IV. FIELD DEPENDENCE OF MAGNETIZATION

According to Ref. 2 in single-crystalline bismuths for $H \| C_3$ the magnetic moment changes almost linearly in the whole field range (except for the lowest one; the small changes are ascribed to the paramagnetic contribution of the impurity charge carriers), being all time diamagnetic. Figure 3 shows the magnetic moment field dependences in large-angle Bi bicrystals at the magnetic field orientation along the inner boundary plane. As it is seen from the figure, the $m(H)$ curves are characterized by pronounced diamagnetism in weak fields [for temperatures $T < T_c$ the magnetic susceptibility $|\chi|$ sharply increases (Fig. 3, inset *a*) when the magnetic field decreases], by paramagnetic maximum (in the magnetic field region 0.5–2 kOe), a weak dependence on temperature, and almost a linear change at $H > 2$ kOe (Fig. 3, inset *b*). The diamagnetism increase in Bi bicrystals at $H < 0.5$ kOe and at low temperatures is explained not only by the disappearance of the paramagnetic contribution of the impurity carriers, but also by the CI transition into the superconducting state. An observation of the well-pronounced Meissner effect confirms the fact that on the inner boundary there is the superconducting material in the amount sufficient for the influence on the magnetic moment value.

Figure 4 shows the results of measurements of the magnetic hysteresis loop at 2 K in one of the samples of large-angle bicrystals with the CI of a twisting type. The magnetic hysteresis loop clearly shows the behavior typical for strong type-II superconductors and becomes reversible above 2.5 kOe at the irreversibility field, which is a few times lower than the upper critical field H_{c2} of both superconducting phases at this temperature. The magnetization curve at 2 K exhibits a large hysteresis; at zero applied field the remnant moment is significant and the magnetic hysteresis loop is almost symmetric.The screening effects in the interfacial plane are expected to be rather weak, since the interfacial thickness is somewhat less than 2λ (λ is the penetration depth).

V. CONCLUSIONS

We have investigated magnetic properties of large-angle bismuth bicrystals with crystallite interfaces of twisting types and have found two new superconducting phases ($T_c \sim 8.4$ K and $T_c \sim 4.3$ K), which might be associated with the central part and the adjacent layers of the crystallite interface. These phases have a similar structure, but their electronic properties are different in both superconducting and normal states.

An observation of two new (stable under atmospheric pressure) superconducting phases on the inner boundary in large-angle Bi bicrystals results from the structural reconstruction under the influence of twisting deformations of the rhombohedral crystal structure *A*7. This modification of bismuth differs in parameters from high pressure phases Bi11-Bi1V,[8] metastable phases[9] obtained in ultrathin layers, granular systems consisting of rhombohedral clusters,[10,11] and nanoparticles.[12]

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